

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
18 April 2002 (18.04.2002)

PCT

(10) International Publication Number  
**WO 02/30477 A1**

(51) International Patent Classification<sup>7</sup>: **A61L 9/00**,  
9/01, 9/04, 11/00

(21) International Application Number: PCT/US01/31641

(22) International Filing Date: 9 October 2001 (09.10.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/685,963 10 October 2000 (10.10.2000) US

(71) Applicants: AUBURN UNIVERSITY [US/US]; Auburn,  
AL 36849-5312 (US). HALOSOURCE CORPORA-  
TION [US/US]; 3005 First Avenue, Suite 300, Seattle,  
WA 98121 (US).

(72) Inventors: WORLEY, Shelby, D.; 410 Dixie Drive,  
Auburn, AL 36832 (US). BROUGHTON, Royall,  
M.; 440 Cross Creek Road, Auburn, AL 36832 (US).  
WILLIAMS, Jeffrey, F.; 3013 Meinhold Road, Langley,  
WA 98260 (US).

(74) Agent: CRUZ, Laura, A.; Christensen O'Connor Johnson  
& Kindness PLLC, Suite 2800, 1420 Fifth Avenue, Seattle,  
WA 98101 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM,  
HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,  
LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,  
MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL,  
TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,  
TG).

**Published:**

- with international search report
- before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments

*For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.*

(54) Title: USE OF N-HALAMINE BIOCIDAL POLYMER FOR ODOR CONTROL

(57) Abstract: The present invention is a method of using a polymeric N-halamine biocidal material as an agent preferably used in conjunction with a matrix material for the reduction of noxious odors caused by the decomposition of organic compounds. In a preferred embodiment of the method according to the present invention, the biocidal N-halamine polymer is provided in a comminuted form and mixed with super absorbent polymer to provide a treatment composition. The treatment composition is emplaced within an article to provide intimate contact between the composition and a microorganism-containing fluid. The fluid is absorbed by the super absorbent polymer thereby providing a surface for the biocidal polymer to contact the microorganism.

WO 02/30477 A1

## USE OF N-HALAMINE BIOCIDAL POLYMER FOR ODOR CONTROL

### Field of the Invention

The present invention relates to a method of using N-halamine biocidal polymer for the purpose of modulating the activity of microorganisms such as bacteria, fungi, and yeasts to cause a reduction of the noxious odors in articles such as disposable diapers, incontinence pads, bandages, sanitary napkins, pantliners, sponges, animal litter, carpets, fabrics, and air filters.

### Background of the Invention

A variety of microorganisms such as certain bacteria, fungi, and yeasts are capable of aiding the decomposition of bodily fluids such as urine and blood, or in the formation of biofilms, which produce undesirable odors in commercial products. For example, bacteria such as *Bacterium ammoniagenes* and *Proteus mirabilis* are known to accentuate the decomposition of urea to form noxious ammonia gas through a urease enzyme catalysis mechanism. See U.S. Patent No. 5,992,351. If an effective treatment composition for disrupting (inhibiting) the urease action can be found, the undesirable odor created by ammonia gas can be minimized. By effective, the treatment composition should be insoluble to resist migrating to human skin, cost effective to be commercially viable, and stable to withstand long periods of shelf life, such as is suitable for consumer uses.

Conventional treatments have been reported for the reduction of odors caused by microorganisms containing urease. One treatment method involves the use of quaternary ammonium compounds. See *J. Pediatrics* 39:730 (1951) and U.S. Patent Nos. 5,981,668 and 6,017,561. Another treatment method involves the use of biocidal biguanides. See *J.S.D.C.* 113:48 (1997) and *Tex. Chem. & Color.* 28:28 (1996). Another treatment method involves the use of bacteriostatic boron compounds. See U.S. Patent Nos. 4,949,672; 5,176,108; 5,944,704; and 5,992,351. A further treatment method involves the use of guanidine salt urease inhibitors. See U.S. Patent Nos. 4,957,063; 5,097,799. And yet another treatment method involves the use of absorbent carbon particles. See U.S. Patent No. 5,951,744. And a further treatment method involves the use of cyclodextrin complexing agents. See U.S. Patent Nos. 5,429,628; 5,714,445. And finally, another treatment method involves the use of urease negative bacteria. See U.S. Patent Nos. 5,507,250; 5,634,431. While these methods can provide at least partial relief

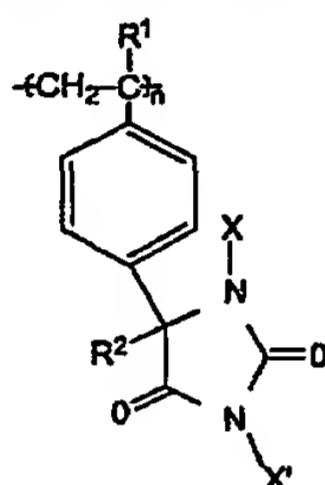
from the noxious odors, there are disadvantages with each method including commercial nonviability, skin sensitivity and possibly respiratory problems for the user.

### Summary of the Invention

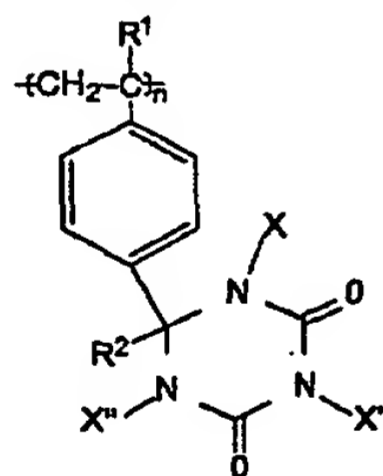
The present invention is a method of using a polymeric N-halamine biocidal material as an agent preferably used in conjunction with a matrix material for the reduction of noxious odors caused by the decomposition of organic compounds.

Suitable biocidal materials suitable for use in the present invention include polymeric cyclic N-halamine biocidal compounds, such as those biocidal polymers including a monomeric repeating unit of one or more structures I, II, III, IV, V, VI, VII, VIII, or IX:

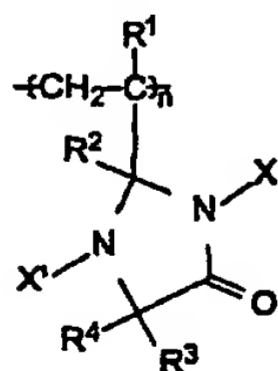
#### STRUCTURE I:



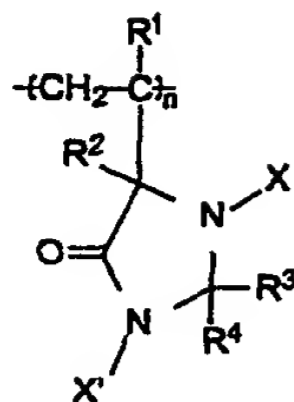
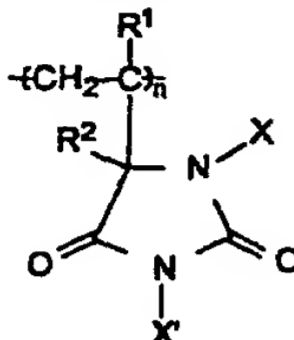
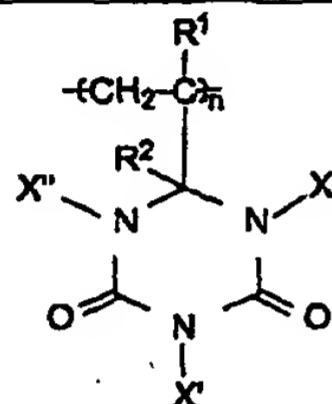
#### STRUCTURE II:



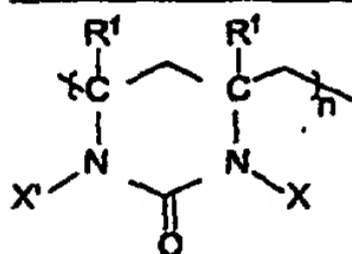
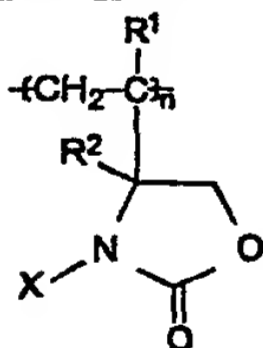
#### STRUCTURE III:



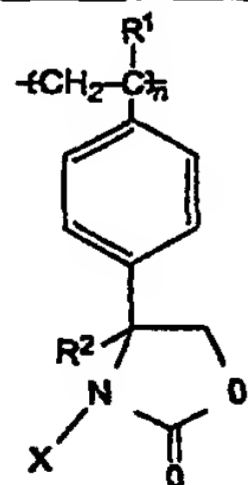
#### STRUCTURE IV:

STRUCTURE V:STRUCTURE VI:

5

STRUCTURE VII:STRUCTURE VIII:

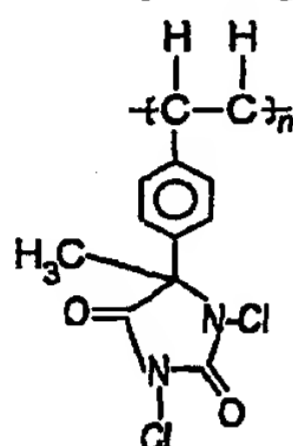
10

STRUCTURE IX:

wherein  $X$ ,  $X^I$  and  $X^{II}$  are independently chlorine, bromine or hydrogen, provided that at least one of  $X$ ,  $X^I$  and  $X^{II}$  is chlorine or bromine;  $R^1$  is a hydrogen or  $C_1$  to  $C_4$  alkyl;  $R^2$  is  $C_1$ - $C_4$  alkyl, benzyl or  $C_1$ - $C_4$  alkyl-substituted benzyl; and  $R^3$  and  $R^4$  are

independently C<sub>1</sub>-C<sub>4</sub> alkyl, phenyl, C<sub>1</sub>-C<sub>4</sub> alkyl-substituted phenyl, benzyl or C<sub>1</sub>-C<sub>4</sub> alkyl-substituted benzyl, or R<sup>3</sup> and R<sup>4</sup> together form a pentamethylene or tetramethylene moiety.

A preferred biocidal material used in the present invention is  
 5 poly-1,3-dichloro-5-methyl-5-(4'-vinylphenyl)hydantoin which is an inexpensive derivative of poly-styrene, and which was first described in U.S. Patent No. 5,490,983, the disclosure of which is hereby expressly incorporated by reference. A monomer unit is represented by the graphical formula:



10 The biocidal properties of poly-1,3-dichloro-5-methyl-5-(4'-vinylphenyl) hydantoin have been recognized to be useful in water filters. See *Ind. Eng. Chem. Res.* 33:168 (1994); *Water Res. Bull.* 32:793 (1996); *Ind. Eng. Chem. Res.* 34:4106 (1995); *J. Virolog. Meth.* 66:263 (1997) *Trends in Polym. Sci.* 4:364 (1996); *Water Cond. & Pur.* 39:96 (1997). But to date, the biocidal polymer has not been applied in a matrix  
 15 material which provides numerous advantages over the conventional use in water filters. The method of using the biocidal polymer according to the present invention includes providing a quantity of the biocidal polymer, then combining the polymer with a fluid permeable or absorptive matrix material to make a treatment composition. The treatment composition can then be placed in an article or container to bring the biocidal polymer in  
 20 intimate contact with a microorganism-containing fluid. In a preferred embodiment of the method according to the present invention, the biocidal N-halamine polymer is provided in a comminuted form and mixed with an absorbent polymer, such as super absorbent polymer to provide a treatment composition. The treatment composition is placed within an article to provide intimate contact between the composition and a  
 25 microorganism-containing fluid, which may be a gas or liquid. The fluid is absorbed by the super absorbent polymer thereby providing a surface for the biocidal polymer to contact the microorganism.

In yet another aspect of the present invention, the biocidal polymer can be coated or imbedded onto the matrix material, such as on a fiber, to provide for control against odor-causing microorganisms.

5 The method according to the present invention is effective against a broad spectrum of pathogens including *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Escherichia coli*, *Candida albicans*, *Klebsiella terrigena*, and rotavirus, among others, causing large log reductions in contact times of the order of a few seconds in water disinfectant applications. Furthermore, it is effective at pH values at least in the range of about 4.5 to about 9.0 and at temperatures at least in the range of about 4°C to  
10 about 37°C, and it is capable of action even in water containing heavy chlorine demand caused by bioburden.

The biocidal polymer used in the method of the present invention is insoluble in water and organic compounds and will thus not migrate in liquid media. It is stable for long periods of time in dry storage (a shelf life of at least one year at ambient  
15 temperature) and can be produced on an industrial scale. Furthermore, all evidence obtained to date suggests that the material is non-toxic and non-sensitizing to humans and animals upon contact.

The present invention thus provides a solid-state biocidal material which is effective against odor-causing microorganisms, insoluble in bodily fluids so as not to  
20 migrate to skin surfaces, stable to withstand lengthy shelf life, non-toxic and non-irritating, and cost effective to be commercially viable.

#### Detailed Description of the Preferred Embodiment

The present invention may be understood more readily by reference to the following detailed description of specific embodiments and the examples included  
25 therein.

As used herein, "the biocidal polymer" refers to an insoluble N-halamine polymer, including those described in U.S. Patent No. 5,490,983, and preferably is poly-1,3-dichloro-5-methyl-5-(4'-vinylphenyl)hydantoin, although this is not meant to be limiting, as any other insoluble N-halamine polymer provides some degree of odor-  
30 limiting capacity.

The biocidal polymer to be used according to this invention is preferably mixed in powder or granular form with an absorbent or filler material to provide a treatment

composition. The absorbent material preferably is a superabsorbent polymer such as ASAP 2000, sold by the Chemdal Corporation of Palatine, Illinois. However, other absorbent materials such as cellulose, diatomaceous earth, cotton, synthetic and natural carpet fibers, cotton or synthetic filter materials can be used. The biocidal polymer preferably comprises a weight percent of about 0.1 to about 5.0 of the treatment composition, and more preferably about 0.5 to about 1.0 for applications involving contact between the treatment composition and human or animal bodily fluids such as occurs in disposable diapers, incontinence pads, bandages, sanitary napkins, pantliners, sponges, and litter. For applications involving contact between the treatment composition and carpets and other textiles the biocidal polymer will be coated on or embedded in the surfaces of the fibers, granules or other matrix surfaces, at preferably a weight percent of about 0.1 to about 2.0, and more preferably about 0.5 to about 1.0. This will be carried out by using an adhesive or by exposure of heat-softened fibers, granules, etc., to powder streams containing the treatment composition. For air filters, coating techniques or simple embedment of particles of the biocidal polymer into available filter material at preferably a weight percent of about 0.1 to about 2.0, more preferably about 0.5 to about 1.0, can be employed. Since many air filters employ a web of synthetic or cellulosic fibers, the treatment composition resides as a substrate rather than a loose material.

The method according to the present invention will reduce noxious odors to a predetermined level by modulating the level of activity of microorganisms which enhance, through catalytic enzymology, the decomposition of organic matter to ammonia or other noxious materials. The biocidal polymer also will reduce noxious odors on fibers or air filters by microorganisms such as those which cause mildew and molds, as well as those from any liquid or aerosol which might contact the surface of these materials. While not intending to be bound to any particular theory, the mechanism through which the biocidal polymer exerts influence over microorganisms is believed to be a result of surface contact of the microorganism with halogen moieties covalently bound to the hydantoin functional groups of the polymer. The halogen atoms are transferred to the cells of the microorganisms where they cause modulation of activity through a mechanism not completely understood, but probably involving oxidation of essential groups contained within the enzymes comprising the organisms. Halogen moieties can include bromine or chlorine.

Preferably, it is contemplated that a broad variety of absorbent and filler materials can be used in conjunction with the biocidal polymer to provide a treatment composition for reducing noxious odors. One purpose of such materials is to enhance contact of fluids, aerosol particles, and solid contaminants with the treatment composition for sufficient periods of time such that the biocidal polymer particles can affect the odor-causing microorganisms. Matrix materials include, but are not limited to: swellable clays, zeolites, alumina, silica, cellulose, wood pulp, fibers, adhesives, coatings and super absorbent polymers or any combination thereof. The treatment composition according to the present invention can further contain adjuvants such as deodorants, fragrances, pigments, dyes, and any combination thereof for cosmetic purposes. The fluid containing the microorganism is preferably flowed through or absorbed by the resulting matrix.

One advantage of the biocidal polymer of this invention over conventional odor-control technology is that the present invention is a more effective biocide against pathogenic microorganisms encountered in medical applications such as *S. aureus* and *P. aeruginosa* than are commercial biocides such as the quaternary ammonium salts. Preferably, the treatment composition can serve a dual function, *i.e.*, modulation of odor-causing microorganisms and of disease-causing pathogens. For this reason the treatment composition of the present invention will have widespread use in hospital settings.

It should be understood that the practice of this invention applies to odors generated by microorganisms in both human and animal fluids as well as to airborne and waterborne microorganisms.

The present invention is more particularly described in the following examples, which is intended as illustrative only since numerous modifications and variations therein will be apparent to those skilled in the art.

25

## EXAMPLES

### EXAMPLE-1

#### Super Absorbent Polymer (SAP)

Super absorbent polymer (SAP) obtained from Chemdal Corp. (Palatine, IL) (ASAP 2000) was mixed with comminuted biocidal polymer, wherein the biocidal polymer was synthesized by the methods outlined in U.S. Patent No. 5,490,983, herein incorporated by reference, in several ratios of weight percentages with 0% biocidal polymer serving as a control. Mixing was accomplished by manually shaking the SAP

and biocidal polymer together in a vial. A 0.25 gram sample of each composition was inoculated with 5.0 milliliters of a challenge suspension containing 10% *Proteus mirabilis* ( $6.7 \times 10^7$  CFU/mL) in phosphate buffered water (pH 7) and 90% supplemented human, female, pooled urine (the supplement was 1.25 grams urea per 25 mL urine). All samples were incubated at 37°C for 6 hours.

An odor test panel including of 13 volunteer nonsmokers evaluated the ammonia odor from the samples after 6 hours of incubation. The volunteers rated the odor on a scale of 0 (no odor) to 10 (strong odor). The averaged results are shown in Table 1. It can be seen in Table 1 that the higher the weight percentage of the biocidal polymer, the lower the average odor rating recorded by the panel.

Weight % Biocidal Polymer x 100%	Mean Panel Odor Rating
0	8.7
0.1	7.8
1.0	2.7
5.0	2.4

Table 1. Qualitative Odor Test Data for Mixtures of the Biocidal Polymer and Super Absorbent Polymer (SAP)

#### EXAMPLE-2

##### Cellulose Diaper Material

Samples of a commercial disposable diaper material (70% cellulose, 30% polyolefin), each weighing about 1 gram, were slurried in 150 milliliters of distilled water in a blender. Then samples of slurried pulp were mixed with biocidal polymer particles (10 to 50  $\mu$ m) such that the blends contained 0.5, 1.0, and 2.5 percent by weight biocidal polymer. After further mixing in the blender, each sample was transferred to a sterile beaker where it was diluted with a 100 mL portion of distilled water rinse. Each pulp/biocidal polymer mixture was vacuum filtered to remove the water and dried for 48 hours. The resulting "paper" samples then contained the biocidal polymer at the three weight percentages given above.

Each paper sample as well as a control sample of the original diaper material containing no biocidal polymer was then inoculated with 1.0 mL of a suspension of about  $1.0 \times 10^8$  CFU/mL of *P. mirabilis* mixed with 5.0 mL of supplemented urine solution

(1.25 grams urea per 25 mL of human, female, pooled urine) in a sterile 250 mL French square bottle. The bottle was constantly aerated with humidified air with any ammonia being produced swept into the bottom of a 1 liter Wheaton bottle containing 1000 mL of ultra-pure water. The water in the Wheaton bottle was stirred constantly with a vortex of about 2 inches. After contact times of 6, 8, 12 and 24 hours, 100  $\mu$ L aliquots were removed and subjected to ammonia analyses using a SIGMA Diagnostics Ammonia Procedure (No. 171-UV). It was determined by an in-house sniff panel that a 35 mg/L solution of ammonia is the minimum concentration level which can be detected by the average human nose. This translates to 2 mg/L using the SIGMA reagent kit on water aliquots from the Wheaton bottle, i.e., 2 mg/L as registered by the test kit in this experiment should be detectable by the human nose.

The results from this experiment are given in Table II. The data show that for the control containing no biocidal polymer ammonia detectable by the human nose was present after 6 hours contact of the bacteria with the paper. Even after 8 and 12 hours the level of ammonia was not detectable by the human nose for any of the paper samples containing the biocidal polymer. After 24 hours contact, the level was detectable for 0.5 and 1.0 weight percent samples, although considerably reduced relative to the control sample. A slightly higher concentration of ammonia was detected for the 1.0 weight percent sample than for the 0.5 one. This anomaly was probably due to a greater bioburden or less uniform mixing of the biocidal polymer with the cellulose in the former. No ammonia could be detected for the sample containing at least 2.5 weight percent biocidal polymer at 24 hours contact. It can be concluded that the latter concentration of biocidal polymer completely inactivated the odor-causing bacteria. It is evident that dispersing the biocidal polymer throughout a paper matrix can lead to reduction, and even elimination, of odor caused by *P. mirabilis*.

Table II. Quantitative Odor Test Data for Mixtures of Biocidal Polymer and Cellulose/Polyolefin

Weight % Biocidal Polymer	Concentration <sup>a,b</sup> of Ammonia Detected at:			
	6 hours	8 hours	12 hours	24 hours

Weight % Biocidal Polymer	Concentration <sup>a,b</sup> of Ammonia Detected at:			
	6 hours	8 hours	12 hours	24 hours
0	2.5	6.0	15.4	59.1
0.5	0	0.42	1.3	9.5
1.0	0	0.63	1.7	12.1
2.5	0	0	0	0

<sup>a</sup>Concentration in mg/L; 2 mg/L is detectable by the human nose under the conditions of the experiment.

<sup>b</sup>The data for the ammonia test are accurate to within  $\pm 0.5$  mg/L.

While the preferred embodiment of the invention has been described, it will be appreciated that various changes can be made therein without departing from the spirit and scope of the invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of controlling the activity of a microorganism in a fluid using N-halamine polymer, comprising:  
providing a quantity of biocidal N-halamine polymer;  
combining the polymer with a matrix material to provide a treatment composition;  
and  
contacting the composition with a microorganism-containing fluid to modulate the activity of the microorganism.
2. The method of Claim 1, wherein the polymer is an insoluble N-halamine polymer.
3. The method of Claim 2, wherein the polymer is poly-1,3-dichloro-5-methyl-5-(4'-vinylphenyl)hydantoin.
4. The method of Claim 1, wherein the matrix material is selected from the group consisting of swellable clays, zeolites, alumina, silica, cellulose, wood pulp, fibers, adhesives, coatings, super absorbent polymers, papers and any combination thereof.
5. The method of Claim 4, wherein the polymer is coated onto any one of the matrix materials.
6. The method of Claim 4, wherein the polymer is imbedded into any one of the matrix materials.
7. The method of Claim 1, further comprising mixing the composition with an adjuvant selected from the group consisting of deodorants, fragrances, pigments, dyes, and any combination thereof.
8. The method of Claim 1, further comprising:  
absorbing the fluid containing the microorganism onto the matrix material thereby providing the contact between the microorganism with the polymer.

9. The method of Claim 1, further comprising emplacing the composition within an article selected from the group consisting of diapers, incontinence pads, bandages, sanitary napkins, pantliners, sponges, litter, carpets, fabrics, and air filters.

10. The method of Claim 1, wherein the polymer comprises an amount of about 0.1 to about 5.0 percent by weight of the composition.

11. The method of Claim 8, wherein the polymer comprises an amount of about 0.5 to about 1.0 percent by weight of the composition.

12. The method of Claim 1, wherein the microorganism is a bacterium, yeast, fungus, protozoan, virus, mold, or algae.

13. The method of Claim 1, wherein the microorganism is a bacterium selected from the group consisting of *Bacterium ammoniagenes* and *Proteus mirabilis*.

14. The method of Claim 1, wherein the fluid is in the liquid phase.

15. The method of Claim 1, wherein the fluid is in the gas phase.

16. The method of Claim 1, wherein the microorganism is a pathogen selected from the group consisting of *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Escherichia coli*, *Candida albicans*, *Klebsiella terrigena*, and rotavirus.

17. The method of Claim 1, wherein the quantity of biocidal polymer is comminuted.

18. The method of Claim 17, wherein the polymer and the matrix material are mixed.

19. The method of Claim 1, wherein the modulating activity occurs to urease enzymes in the microorganism.

20. The method of Claim 1, wherein the pH of the fluid is about 4.5 to about 9.0.

21. The method of Claim 1, wherein the composition is effective at temperatures of about 4°C to 37°C.

22. The method of Claim 1, wherein the polymer has a shelf life of at least one year at ambient temperature.

23. The method of Claim 1, wherein the modulating activity controls noxious odors.

24. A method of using N-halamine polymer, as an odor control agent comprising:

providing a quantity of comminuted biocidal N-halamine polymer,

mixing the biocidal polymer with super absorbent polymer to provide a treatment composition; and

emplacing the composition within an article to provide for contact between a microorganism-containing fluid and the composition, wherein the super absorbent polymer absorbs the fluid thereby providing a surface for contact between the microorganism and the biocidal polymer.

25. An article of manufacture for controlling noxious odors, comprising:

a quantity of comminuted biocidal N-halamine polymer; and

a quantity of super absorbent polymer mixed with the biocidal polymer to provide a treatment composition, wherein the composition is emplaced within the article to provide for contact between the composition and a microorganism-containing fluid wherein the super absorbent polymer absorbs the fluid thereby providing a surface for contact between the microorganism and the biocidal polymer.

26. An article of manufacture for controlling noxious odors, comprising:

a quantity of biocidal N-halamine polymer; and

a fiber wherein the biocidal polymer is coated or imbedded onto the fiber to provide for contact between the polymer and an odor-causing microorganism present in a fluid medium.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/31641

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : A61L 9/00, 9/01, 9/04, 11/00

US CL : 424/76.1, 76.21, 76.4, 76.5, 76.8

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/76.1, 76.21, 76.4, 76.5, 76.8

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
East/West

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,882,357 A (SUN et al) 16 March 1999 (16.03.1999), column 2, lines 40-50, column 3, lines 22-41, column 4, lines 3-37, column 5, lines 1-8, 27-45.	1-6, 8-13, 14-23, 26
Y	US 5,981,668 A (FUJITA et al) 09 November 1999 (09.11.1999), column 2, lines 36-43, column 8, lines 1-12.	7
Y	RD 434,052 A (ANONYMOUS) 10 June 2000 (10.06.2000), Abstract.	24, 25

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

26 November 2001 (26.11.2001)

Date of mailing of the international search report

15 FEB 2002

Name and mailing address of the ISA/US

Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703)305-3230

Authorized officer

Robert M. Joynes

Telephone No. (703) 308-1235

Form PCT/ISA/210 (second sheet) (July 1998)

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
18 April 2002 (18.04.2002)

PCT

(10) International Publication Number  
**WO 02/030477 A1**

(51) International Patent Classification<sup>7</sup>: A61L 9/00,  
9/01, 9/04, 11/00

(21) International Application Number: PCT/US01/31641

(22) International Filing Date: 9 October 2001 (09.10.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/685,963 10 October 2000 (10.10.2000) US

(71) Applicants: AUBURN UNIVERSITY [US/US]; Auburn,  
AL 36849-5312 (US). HALOSOURCE CORPORA-  
TION [US/US]; 3005 First Avenue, Suite 300, Seattle,  
WA 98121 (US).

(72) Inventors: WORLEY, Shelby, D.; 410 Dixie Drive,  
Auburn, AL 36832 (US). BROUGHTON, Royall,  
M.; 440 Cross Creek Road, Auburn, AL 36832 (US).  
WILLIAMS, Jeffrey, F.; 3013 Meinhold Road, Langley,  
WA 98260 (US).

(74) Agent: CRUZ, Laura, A.; Christensen O'Connor Johnson  
& Kindness PLLC, Suite 2800, 1420 Fifth Avenue, Seattle,  
WA 98101 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM,  
HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,  
LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,  
MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL,  
TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,  
TG).

**Published:**

- with international search report
- with amended claims

**Date of publication of the amended claims:** 4 July 2002

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: USE OF N-HALAMINE BIOCIDAL POLYMER FOR ODOR CONTROL

(57) Abstract: The present invention is a method of using a polymeric N-halamine biocidal material as an agent preferably used in conjunction with a matrix material for the reduction of noxious odors caused by the decomposition of organic compounds. In a preferred embodiment of the method according to the present invention, the biocidal N-halamine polymer is provided in a comminuted form and mixed with super absorbent polymer to provide a treatment composition. The treatment composition is emplaced within an article to provide intimate contact between the composition and a microorganism-containing fluid. The fluid is absorbed by the super absorbent polymer thereby providing a surface for the biocidal polymer to contact the microorganism.

## AMENDED CLAIMS

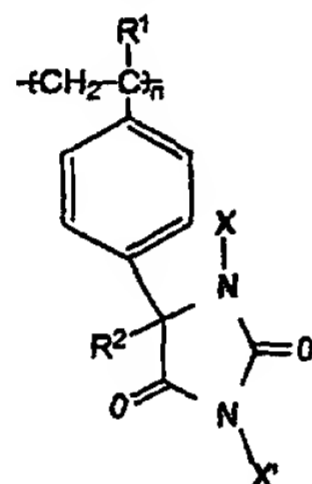
[received by the International Bureau on 11 April 2002 (11.04.02);  
original claims 27-32 amended (3 pages)]

27. A method for making a biocidal composition, comprising mixing a biocidal N-halamine polymer with a matrix material.

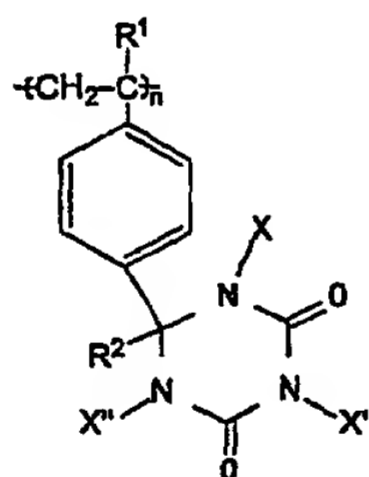
28. A composition, comprising a biocidal N-halamine polymer mixed with a matrix material.

29. A composition, comprising:  
a polymer comprising a structure selected from

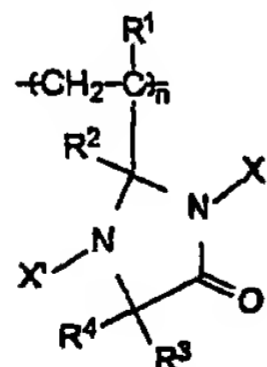
STRUCTURE I:



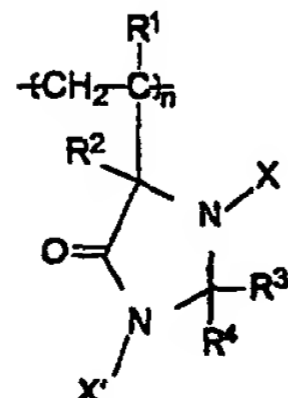
STRUCTURE II:



STRUCTURE III:

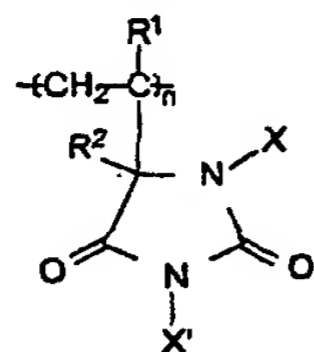


STRUCTURE IV:

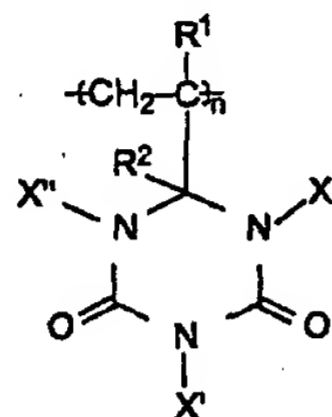


AMENDED SHEET (ARTICLE 19)

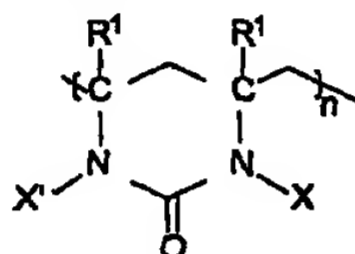
STRUCTURE V:



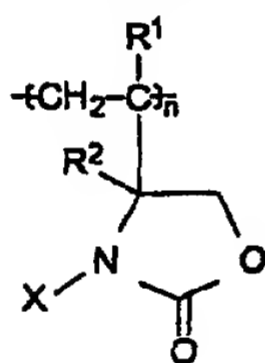
STRUCTURE VI:



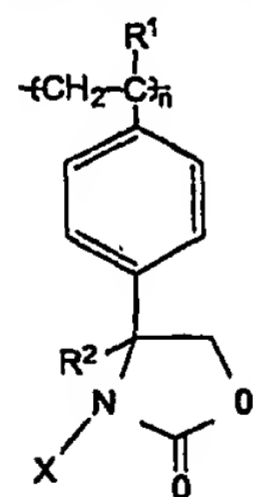
STRUCTURE VII:



STRUCTURE VIII:



STRUCTURE IX:



wherein X, X<sup>I</sup> and X<sup>II</sup> are independently chlorine, bromine or hydrogen, provided that at least one of X, X<sup>I</sup> and X<sup>II</sup> is chlorine or bromine; R<sup>1</sup> is a hydrogen or C<sub>1</sub> to C<sub>4</sub> alkyl; R<sup>2</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl, benzyl or C<sub>1</sub>-C<sub>4</sub> alkyl-substituted benzyl; and R<sup>3</sup> and R<sup>4</sup> are independently C<sub>1</sub>-C<sub>4</sub> alkyl, phenyl, C<sub>1</sub>-C<sub>4</sub> alkyl-substituted phenyl, benzyl or C<sub>1</sub>-C<sub>4</sub> alkyl-substituted benzyl, or R<sup>3</sup> and R<sup>4</sup> together form a pentamethylene or tetramethylene moiety, wherein said polymer is mixed with a matrix material.

30. A composition, comprising poly-1,3-dichloro-5-methyl-5-(4'-vinylphenyl) hydantoin mixed with a superabsorbent polymer.

31. A composition, comprising poly-1-chloro-5-methyl-5-(4'-vinylphenyl) hydantoin mixed with a superabsorbent polymer.

32. A method for controlling odor, comprising mixing biocidal N-halamine polymer with a matrix material.

CORRECTED VERSION

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
18 April 2002 (18.04.2002)

PCT

(10) International Publication Number  
WO 02/030477 A1

(51) International Patent Classification<sup>7</sup>: A61L 9/00,  
9/01, 9/04, 11/00

(21) International Application Number: PCT/US01/31641

(22) International Filing Date: 9 October 2001 (09.10.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/685,963 10 October 2000 (10.10.2000) US

CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM,  
HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,  
LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX,  
MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL,  
TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,  
TG).

(71) Applicants: AUBURN UNIVERSITY [US/US]; Auburn,  
AL 36849-5312 (US). HALOSOURCE CORPORA-  
TION [US/US]; 3005 First Avenue, Suite 300, Seattle,  
WA 98121 (US).

Published:  
— with international search report  
— with amended claims

(72) Inventors: WORLEY, Shelby, D.; 410 Dixie Drive,  
Auburn, AL 36832 (US). BROUGHTON, Royall,  
M.; 440 Cross Creek Road, Auburn, AL 36832 (US).  
WILLIAMS, Jeffrey, F.; 3013 Meinhold Road, Langley,  
WA 98260 (US).

Date of publication of the amended claims: 4 July 2002

(74) Agent: CRUZ, Laura, A.; Christensen O'Connor Johnson  
& Kindness PLLC, Suite 2800, 1420 Fifth Avenue, Seattle,  
WA 98101 (US).

(48) Date of publication of this corrected version:  
6 September 2002

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,

(15) Information about Correction:  
see PCT Gazette No. 36/2002 of 6 September 2002, Sec-  
tion II

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: USE OF N-HALAMINE BIOCIDAL POLYMER FOR ODOR CONTROL

(57) Abstract: The present invention is a method of using a polymeric N-halamine biocidal material as an agent preferably used in conjunction with a matrix material for the reduction of noxious odors caused by the decomposition of organic compounds. In a preferred embodiment of the method according to the present invention, the biocidal N-halamine polymer is provided in a comminuted form and mixed with super absorbent polymer to provide a treatment composition. The treatment composition is emplaced within an article to provide intimate contact between the composition and a microorganism-containing fluid. The fluid is absorbed by the super absorbent polymer thereby providing a surface for the biocidal polymer to contact the microorganism.

WO 02/030477 A1